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Biofuels Combustion

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Abstract

Major features are described of current research in renewable fuels derived from plants and from fatty acids. Recent and ongoing fundamental studies of biofuel molecular structure, oxidation reactions, and chemical properties of biofuels are reviewed, in addition to combustion applications of biofuels in the major types of engines where biofuels are used. Biofuels and their combustion are compared with combustion features of conventional petroleum-based fuels. Two main classes of biofuels are described, those consisting of small, primarily alcohol, fuels, particularly ethanol, n-butanol and iso-pentanol, that are used primarily to replace or supplement gasoline, and biodiesel fuels derived from fatty acids and are used primarily to replace or supplement conventional diesel fuels. Research efforts on so-called second- and third-generation biofuels are discussed briefly.

Keywords: ethanol, iso-pentanol, biodiesel, methyl esters, combustion

Key Terms

Autoignition: spontaneous ignition of a fuel/oxidizer mixture, without external source of ignition

Biodiesel: fuel produced via transesterification of plant oils and fats

Equivalence ratio: ratio of fuel concentration to the fuel concentration that would consume all of the available oxygen

HCCI: Homogeneous Charge, Compression Ignition, a new class of engine with good economy and emissions properties

NO_x: oxides of nitrogen, generally harmful engine emissions that are major sources of smog and air pollution

Surrogate fuel: a mixture of a few fuel species intended to represent a much more complex fuel mixture

ACRONYMS

CN: cetane number

FAME: Fatty acid methyl ester

HCCI: Homogeneous Charge, Compression Ignition

ON: octane number

SI: Spark-Ignition

Summary Points

1. Biofuels are more like conventional petroleum-based fuels than they are different
2. Biofuels intended to replace gasoline are primarily small molecule alcohols, including ethanol, n-butanol and iso-pentanol
3. Biodiesel fuels are in exactly the same molecule size and shape range as conventional diesel fuels
4. Differences between performance and emissions from biofuels and conventional fuels are relatively small, but they need to be understood
5. Nuances in biodiesel fuel composition translate into different performance metrics, such as cetane number
6. We have the tools, experimental, theoretical, modeling, etc., to evaluate any proposed biofuel or other fuel that is suggested for study

Brief annotations of bibliographical references

ref 3: Very deep, thorough review of details of biodiesel fuel chemistry. Chemistry, not combustion.

ref 4 and 5: these multidisciplinary centers are likely to revolutionize fuel research. Each represents a critical mass of researchers

ref 20: biofuels Bible, huge collection of valuable material

ref 26: Very impressive synthesis of the entire chain from plants to processing, storage, combustion

ref 44: first complete kinetic model for biodiesel, explains kinetics of C=C double bonds

ref 50: discusses bioengineering to genetic modification of the plant to make a better biofuel

ref 58: paper made a long leap from unsaturation to engine performance

ref 76 and 77: experimental observation and kinetic explanation of the effect of oxygen on soot reduction in diesel engines

ref 85: thorough explanation of the effects of biodiesel fuel on NO_x emissions

INTRODUCTION

Many factors are contributing to growing world-wide interest in biofuels and their combustion properties. Steadily growing costs of petroleum and a desire for energy security in countries with limited petroleum resources are common concerns. Eventual depletion of petroleum reserves has been predicted for many years [1,2] and is inevitable, although new reserves continue to be discovered, and biofuels offer opportunities to extend the petroleum era, both as blending agents with petroleum fuels or as complete replacement fuels. Atmospheric emissions of greenhouse gases, especially carbon dioxide, and other pollutant chemicals from combustion of fossil fuels are a very serious world-wide problem, and biofuels produced largely from atmospheric carbon dioxide and sunlight represent renewable, "carbon neutral" fuels.

Common biofuels [3] include small-molecule alcohols such as ethanol, butanol or iso-pentanol produced from sugars or starch, as well as large-molecule biodiesel fuels produced from vegetable oils or fats that have been converted into fatty acid methyl or ethyl esters (FAMEs or FAEEs) via transesterification. A next generation of biofuels are being developed via microbial reactors, intracellular synthesis of hydrocarbons by bacteria, yeasts and fungi, from cellulosic material and lignins, and others, although such fuels are still far from practical use. While many types of biofuels have been identified as possible candidates for widespread use, the only two renewable liquid biofuels in common use are ethanol and biodiesel.

In the interests of accelerating development of the next generation of practical biofuels, large multidisciplinary research centers are being established [4,5] supported by leading universities, national laboratories, and private companies, and these centers represent an important new approach to the many challenges of biofuels. One recent example of the productivity of this approach involves microbial

production of iso-pentanol at the Joint BioEnergy Institute [6-8], with a parallel research effort on characterizing the performance of iso-pentanol in internal combustion engines [9]. The engine work showed that iso-pentanol had combustion performance similar to ethanol and gasoline but also had some important advantages over smaller alcohol fuels, especially ethanol, including higher volumetric energy density, greater miscibility with water, and better material compatibility with elastomers. Similar coordinated fundamental and engine studies at the RWTH-Aachen center for Tailor-Made Fuels from Biomass [5] of 2-methyl tetrahydrofuran, combining engine ignition and emissions evaluations of soot and NO_x [10] with synthesis of the fuel from lignocellulose [11]. This is a quite different approach to the concept of directly pyrolysing wood and biomass that has been pursued previously [12]. This multidisciplinary approach is a new model for management of research in biofuels research.

PROPERTIES OF BIOFUELS

Biofuels are qualitatively different from petroleum-based fuels in that they consist of only one or a few different components. Neat ethanol, n-butanol, or iso-pentanol used as gasoline replacements consist of a single type of molecule, while gasoline contains many hundreds of different hydrocarbon species. Similarly, petroleum-based diesel fuel contains hundreds or thousands of different chemical species, while biodiesel fuels contain only 5 or 6 different chemical species. The complexity of practical petroleum-based fuels makes it impossible to include all of its components, either in an experimental test fuel or in a computational model fuel, necessitating "surrogate" fuel mixtures to reduce the complexity of test fuels [13-19]. In contrast, all components of a typical biofuel can be included in experimental or kinetic modeling analyses.

Most biodiesel fuel consists of mixtures of the same FAME species [20-28], including methyl stearate (C18:0), methyl oleate (C18:1), methyl linoleate (C18:2), and methyl linolenate (C18:3), all

based on a straight chain of 18 carbon atoms but with zero, one, two and three C=C double bonds in the carbon chain, together with the slightly smaller saturated component methyl palmitate (C16:0). In this notation, CX:B denotes a methyl ester with X carbon atoms in the chain, with B C=C double bonds in the chain. These species are shown schematically in Figure 1.

Among the FAMES based on these components are methyl esters of soy, sunflower, safflower, linseed, jatropha, cottonseed, corn, olive, palm, peanut and rapeseed oils, as well as beef tallow, and the relative fractions of the 5 components are shown in Table 1. These fuels also contain very small levels (i.e., not more than 1-2% total) of other methyl ester species that make minimal contributions to their combustion properties. Methyl ester from Camelina oil contains nearly 85% of these 5 components, with about 12% of C20:1; Camelina is interesting because it requires little fertilizer, tolerates cold weather, has higher vegetable oil yield than soybeans [29] and grows well in semi-arid regions with poor soils. Research has been carried out on production of plant oils that can be produced by microalgae [30] and processed into biodiesel fuel. Although this is an apparently attractive process because of its independence of land use and efficiency in cultivation, it remains an extremely small source of biofuels. A very interesting analysis of the microbiology of polyunsaturated fatty acids and the genetics involved in their synthesis is available from Wallis et al. [31]. Also shown are values of Cetane Number (CN) for each of these fuels, based primarily on engine and laboratory experimental measurements [32-34].

The limited number of components of biodiesel fuel makes it especially urgent and productive to study them in detail, either separately or combined into actual biodiesel fuels, using a variety of techniques to cover as broad a range of reactive parameters as possible. In recent experimental studies in a jet-stirred reactor, Battin-Leclerc et al. studied oxidation of methyl oleate [35] and methyl palmitate

[36], and Campbell et al. [37] used an aerosol shock tube [38,39] to study ignition of methyl oleate and methyl linoleate. Those experiments have provided data for testing subsequent kinetic modeling studies by Herbinet et al. [40] using the EXGAS automated mechanism generation technique [41] for reaction mechanisms of the saturated biodiesel components, and by Westbrook et al. [42-44] using manually developed kinetic reaction mechanisms for all 5 biodiesel components. The ability to model oxidation of all 5 components means that this computational tool can be used to study biodiesel fuels derived from any of the oil sources listed in Table 1. Dagaut et al. studied oxidation of rapeseed methyl ester [45] and explored using a kinetic mechanism for n-hexadecane as a surrogate for the saturated methyl ester, with generally positive results [46]. Fatty acid methyl and ethyl ester combustion has also been studied in recent experiments in motored engines [47,48] and microgravity [49].

Biodiesel fuels have several significant advantages over conventional diesel fuels [50,51]. These advantages include faster biodegradation, important in environmentally sensitive areas, a higher flashpoint, which provides better safety in fuel handling, reduced fuel toxicity, and increased lubricity. In addition, biodiesel does not contain sulfur or aromatic species which are common in many diesel fuels and lead to engine problems and toxic emissions, and biodiesel fuel generally has lower CO and soot emissions than conventional diesel fuel.

Disadvantages of some biodiesel fuels include poor cold-temperature properties and oxidative instability of the fuel when stored. The carbon chain length and the number of C=C double bonds in each of the 5 biodiesel components lead to different physical properties. Saturated methyl esters condense at temperatures much higher than those with one or more C=C double bonds, so biodiesel fuels with large fractions of saturated methyl esters become gel-like and do not flow properly at low operating temperatures or in cold climates. In contrast, biodiesel fuels with multiple C=C double bonds flow well at low temperatures but react much more rapidly than those with high saturated fractions

when they are stored for any length of time. For example, Durrett et al. [51] cite studies in which esters of linoleate react 40 times faster than oleate esters [52,53] and attribute this large difference to the weakly bound H atoms in the *bis*-allylic methylene group between two double bonds in both methyl linoleate and linolenate. Similarly, Moser and Vaughn [29] note that camelina methyl ester fuel, which contains about 20% C18:2 and 33% C18:3, must be blended with another methyl ester with higher saturation or with antioxidant additives in order to be sufficiently stable to resist excess oxidation during storage. The products of this oxidation increase the viscosity of the biodiesel fuel and cause plugging of filters and fouling of fuel injectors. Other recent studies of biodiesel fuel thermal stability provide consistent insights [54-56]. This inverse relation between cold flow and oxidative stability [50] can make it difficult to find an optimal biodiesel fuel composition, based on naturally occurring oils. Kinney and Clemente discuss efforts to use mutational breeding to decrease the saturated content of soybean oil and simultaneously inhibit conversion of soybean oil's oleic acid to linoleic acid to maximize the methyl oleate in the resulting biodiesel fuel, to improve cold temperature properties and reduce fuel oxidation under storage conditions.

The average amount of unsaturation of methyl ester fuels, a quantity called the Iodine Number (IN), is defined experimentally as the mass of iodine in grams that is consumed by 100 grams of a given chemical substance. Double bonds in methyl esters react with iodine, so the IN of a methyl ester fuels is an experimental measure of the number of C=C double bonds in each fuel. A similar measure can be called the Double-bond Number (DN) which is counted in each fuel by multiplying the fractions of each component in Table 1 by the number (i.e., 0, 1, 2, or 3) of double bonds in each component [44], and these totals are shown as DN in Table 1. Knothe [57] and Benjumea et al. [58] continue to extend the concept of IN to methyl ester fuels with more than one C=C double bond and count up the number of allylic sites in a given methyl ester component as well as the *bis*-allylic position equivalent (BAPE), which

is the number of bis-allylic sites in each methyl ester component. They then use these structural measures to correlate these indices with combustion properties of the different biodiesel fuels, explaining that higher IN values and higher fractions of bisallylic sites generally result in lower Cetane Number (CN), higher NO_x emissions, higher total hydrocarbon emissions and soot emissions. We will return to these double bond correlations below to review analyses of these bis-allyl bonds in biodiesel fuels in more fundamental terms.

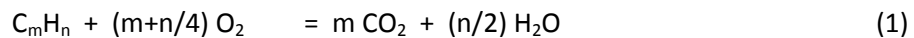
ENGINES

It is difficult to discuss fuels and biofuels without similarly discussing the engines or other systems that burn those fuels. Biofuels have largely been approached as supplements or replacements for petroleum-based fuels developed for use in specific types of engines or burners. In Figure 2, three common classes of internal combustion engines are illustrated, including the spark-ignition (SI) gasoline engine, compression ignition (CI) diesel engine, and a hybrid type of engine, a Homogeneous Charge, Compression Ignition (HCCI) engine. Not shown is another important engine class, the gas turbine jet engine used primarily for aircraft propulsion, that has always burned petroleum-based fuels but is being adapted for biofuels.

The SI engine uses lighter constituents in petroleum, those with about 4 to 10 C atoms per molecule, jet fuel uses the size range with about 10 - 14 C atoms, and diesel uses the larger molecules with about 15 - 22 C atoms. Each type of engine exploits the physical and chemical properties of the fuels it burns; the smaller alcohol biofuels have molecular weights and other properties similar to those of SI engine gasolines, and most properties of biodiesel fuel are very similar to those of petroleum diesel fuel, so those are the engines most suitable for those particular biofuels. When a biofuel is required as a

replacement or supplement for jet fuel, most often biodiesel fuel is hydrotreated to reduce the fuel molecular weights into the range most suitable for jet fuel [59].

For those unfamiliar with common combustion terms, two terms are useful. A fuel with 'm' carbon atoms and 'n' hydrogen atoms has a corresponding number of O atoms that would oxidize the fuel exactly to CO₂ and H₂O. For the fuel C_mH_n, the number of O atoms can be calculated as:



so for heptane C₇H₁₆, 11 O₂ molecules will burn it exactly to 7 CO₂ and 8 H₂O molecules, and for methyl oleate C₁₉H₃₆O₂, a stoichiometric amount of oxygen would produce 19 CO₂ + 18 H₂O, but since there are already 2 O atoms in the methyl oleate fuel, only 27 O₂ molecules are needed to consume the fuel.

A "stoichiometric" fuel/oxidizer mixture has exactly the number of O₂ molecules to consume the fuel completely to CO₂ and H₂O. The "equivalence ratio", denoted by the symbol 'φ', describes the ratio of the amount of fuel actually being burned to the stoichiometric amount of fuel in the system being described. A "fuel rich" mixture has more fuel than the available oxidizer can consume, so φ > 1.0, and a "fuel lean" mixture has an excess of oxidizer, with φ < 1.0.

Gasoline Engines and Biofuels

Smaller biofuels, primarily alcohols including ethanol, methanol, n-butanol, and iso-pentanol, are well suited for use in SI engines. Their general combustion properties are very similar to those of gasoline, and the most common obstacles to conversion of gasoline engines to use ethanol or methanol have been corrosion of fuel lines, filters and gaskets by the alcohol fuel, problems that have usually been solved by using different materials for those engine and fuel system components. SI engines require a fuel [60] which vaporizes easily and mixes rapidly with air, and the small oxygenated biofuels vaporize

very well. The combustible mixture is ignited by a spark plug and produces a premixed, turbulent flame that propagates across the nearly homogeneous combustion chamber. Ignition occurs primarily in places where the equivalence ratio is close to stoichiometric. Flammability limits and flame speeds for biofuel alcohols are very similar to those of conventional gasoline. SI engine fuels must have acceptable resistance to knocking behavior that occurs if endgas fuel autoignition occurs before the flame can consume all of the fuel/air mixture in the combustion chamber. Knocking behavior is measured by the Octane Number (ON), and fuels with high values of ON resist knock better than fuels with low ON values. All of these biofuel alcohols, in common with gasoline components, have relatively high ON values and therefore are not likely to produce engine knock [61].

Ethanol has an octane number of approximately 100 and strongly resists knocking behavior. One of the early applications for ethanol as an additive to conventional gasoline was in fact to be an anti-knock additive [62]. When the use of tetra-ethyl lead (TEL) was terminated as a gasoline anti-knock additive [63] due to its environmental impacts on ground water, methyl tert-butyl ether (MTBE) was identified as a suitable replacement, but it too had environmental disadvantages [64] due to contamination of ground water. However, many other small oxygenated hydrocarbon species can be quite effective as anti-knocks, and ethanol became and is still widely used in this way, largely due to its absence of serious environmental impacts. Many states in the US now permit as much as 10% ethanol in ordinary gasoline as an antiknock additive.

Ethanol blends with conventional gasoline are now commonly used, with virtually all ratios of ethanol to gasoline. In Brazil, where ethanol is produced in very large quantities from plentiful crops of sugar cane, automobile engines using 100% ethanol have been used widely for many years [2]. The knock resistance of ethanol permits the use of compression ratios significantly higher than those commonly used in gasoline engines, producing better overall combustion efficiencies due to the positive

dependence of combustion efficiency on compression ratio, although NO_x aftertreatment or high levels of exhaust gas recirculation (EGR) are sometimes needed. Widespread use of ethanol automotive fuel from corn has resulted in great attention placed on the social, economic, and political issues involved when crops originally intended to feed people and animals are diverted into fuel production [2,28]. These are factors that favor biofuels production from soils that are not valuable for food crops, from crops that have no competitive markets, or from synthetic processes in artificial facilities that can be situated almost anywhere.

Diesel Engines and Biofuels

Biodiesel fuels, produced from fatty acid methyl esters, have many physical and chemical properties that are similar to those of conventional diesel fuel. In the diesel engine, multiple jets of liquid diesel fuel are injected into high pressure, high temperature air that has been compressed by piston motion [60]. The fuel vaporizes after entering the combustion chamber and mixes with the hot air, leading to ignition.

Until recently, no thoroughly satisfying phenomenological description had been available that integrated the major elements of fuel injection, ignition and combustion in a diesel engine. Dec and collaborators [65] used optical diagnostics to probe inside a working diesel engine to establish this phenomenological model, which is summarized in Fig. 3 and applies to diesel engines fueled by either conventional diesel fuel or biodiesel fuel. Each fuel jet penetrates across the combustion chamber, vaporizing and entraining hot, compressed air from the chamber into the jet and mixing fuel steadily with the entrained air. This reduces the local equivalence ratio from its initial high value of the pure fuel as fuel mixes with O₂, and it raises the vaporized fuel temperature. Mixed fuel and air then ignite when the local equivalence ratio is still quite rich (i.e., equivalence ratio of 2 - 3). This fuel-rich autoignition

burns all of the oxygen available [65,66] and then stops oxidizing when all of the entrained oxygen is depleted, although the carbon and hydrogen has not yet been converted to CO_2 and H_2O . These hot products of the rich ignition can react further, but since there is no remaining oxygen, they instead react with each other and produce significant amounts of soot, which is finally consumed at the interface between the hot ignition products and the surrounding air. The products of the rich premixed burn determine the structure of the soot that is formed, and since biodiesel fuel is not identical to petroleum-based fuel, it is likely that the soot produced from burning biodiesel fuels will also be different. The relationship between the products of the rich premixed burn and the soot that is produced has not been established even for diesel fuel, so the characteristics of the soot produced from biodiesel fuel has been largely unstudied.

The premixed, rich ignition can be seen in blue in Fig. 3, and the soot oxidation "burnout" that occurs at the periphery of the entire spray zone consumes the remaining soot and other unburned hydrocarbons. The time delay between fuel injection and ignition depends sensitively on the size and structure of the fuel molecules. The ignition of a diesel fuel is defined by its Cetane Number (CN), with a high CN indicating rapid ignition and a low CN indicating slow ignition. One area in which biodiesel fuels are significantly different from conventional diesel fuel is the fact that most of its components have one or more C=C double bonds, which have a strong effect on the ignition rate and will be discussed further below.

A second chemical factor that is unique to biodiesel fuels arises from the presence of a methyl ester group at one end of the carbon chain, seen in all 5 components seen in Fig. 1. Most important, the

presence of two O atoms within the fuel molecule makes these molecules "oxygenated" and has important implications about the sooting behavior of biodiesel fuel, as also discussed below.

Finally, there is an interesting niche in which diesel fuel, biodiesel fuel and alcohol fuels, most often butanols but sometimes ethanol, are being blended together to make a different diesel fuel. Two-component mixtures among diesel, biodiesel and alcohols do not mix very well, but mixtures of all three have been found to mix very well and avoid common problems [67,68]. These multicomponent blends are also candidates for HCCI engine fuels, so these 3-component studies could have wide relevance.

HCCI Engine and Biofuels

An important development in recent years [69-72] has been towards a type of hybrid engine intended to combine the advantages of SI and diesel engines without the problems of either. The basic concept, the Homogeneous Charge, Compression Ignition engine (see Fig. 2), is a premixed, spatially homogeneous charge that is fuel-lean and is ignited by piston compression. Because HCCI combustion is premixed, lean and takes place entirely in the gas phase, it avoids soot production that is seen in diesel engines, but it uses a high compression ratio that provides high fuel efficiency [60]. By operating very fuel-lean, the product temperatures remain relatively low, so production of the nitrogen oxides that lead to photochemical smog is sharply reduced. In fact, the basic form of HCCI uses fuel/air mixtures that are too fuel-lean to be able to support a flame, but because most of the charge ignites and burns nearly simultaneously, there is no flame propagation and therefore no opportunity for knocking operation to occur in HCCI combustion.

The most significant difficulty with HCCI and other extremely lean combustion systems is that they are usually subject to unacceptably high emissions of unburned hydrocarbons and CO. This is a common problem that is related to the low NO_x emissions. If combustion temperatures are kept low to limit production of NO_x, then the same low temperatures slow the overall consumption of hydrocarbons and CO. If the combustion temperature is increased, often by increasing the rate of fuel addition, then the temperatures rise and increase NO_x production. For example, Sjöberg and Dec carried out HCCI engine studies using ethanol as their fuel [73] and quantified the influences of EGR on NO_x production, noting that their results also applied to SI combustion of ethanol.

HCCI engines have the attractive feature of being suitable for almost any type of fuel, from diesel fuel to gasolines, and they are capable of burning virtually any biofuel with high efficiency and low NO_x emissions. An interesting extension of this concept is to use two fuels in the same engine, first

injecting a small portion of a fuel that ignites easily (i.e., with high CN), such as a diesel fuel, followed by a second injection of another, more difficult to ignite fuel (i.e., high ON). The earlier injected fuel will already be burning when the second injection occurs, which produces a reliable, quite rapid ignition of the second fuel. Reitz [74,75] calls this strategy Reactivity Controlled Compression Ignition (RCCI), and the second fuel in many of their studies have consisted of fuels such as natural gas or ethanol. The earlier injected, more ignitable fuel can be conventional diesel or biodiesel fuel. The use of multiple injections and the flexibility provided by adjusting the timing of the injections, combined with operation at high compression ratios, can produce very low emissions and high combustion efficiency. The RCCI engine, with its excellent performance characteristics and unusually broad fuel tolerance, is a concept that is likely to grow steadily in importance in the coming years.

BIOFUELS AND SOOT REDUCTION

Recent studies have shown that addition of oxygenated species such as ethers, alcohols and esters to diesel fuel can decrease soot emissions from diesel engines [76,77]. The same soot reduction is observed when biodiesel fuel is blended with conventional diesel fuel [78-88]. McNesby et al. [89] studied non-premixed, opposed flow, laminar ethene/air flames and added ethanol to the air side of the flame, resulting in lower production of soot precursors. However, ethanol addition to the fuel side of the flame increased soot precursor production. McNesby et al. also used kinetic modeling to illustrate the differences in reaction pathways with the two oxygenated additive geometries. McEnally et al. [90] studied axially symmetric, coflowing laminar non-premixed flames, with oxygenated additives in the methane fuel stream, showing increased production of soot precursor species, consistent with the experiments and computed results of McNesby et al. All these results confirm the conclusion of Dec et al. [65] that ignition and soot production in a diesel engine is a premixed phenomenon, albeit under

quite fuel-rich conditions. Neat biodiesel fuel produces less soot than conventional diesel fuel under otherwise the same operating conditions, due to the higher level of oxygen in the fuel [84,85].

The amount of soot reduction is approximately linear with the amount of added oxygen, but not all oxygenated additives are equally effective in soot reduction [77,87]. Additives with a single imbedded O atom, like methanol, ethanol, and dimethyl ether, are among the most effective in reducing soot precursor production, per O atom added to the fuel mixture.

However, the conformation of the two O atoms in biodiesel fuels as $R(C=O)OR$ has been found [77,87] to be less effective in soot reduction per O atom added to the fuel, and the key seems to be the decomposition of the $CH_3O(CO)\bullet$ radical primarily to $CH_3 + CO_2$ rather than $CO + CH_3O$ [91,92]. By decomposing in this way, the two O atoms remain bonded to a single C atom. Each O atom must remove a C atom from the reactive pool to reduce soot production, but when two O atoms remain bonded to a single C in the form of CO_2 , these O atoms are less efficient in removing C atoms from the reactive medium [77]. Combustion of methyl esters has been observed to produce "early" CO_2 and this is recognized as a signature of methyl ester oxidation [77,91,92], and this effect is traced to the decomposition of the methoxyformyl radical, $CH_3O(CO)\bullet$.

Studies in diesel engines report that diesel engines using biodiesel fuel produce slightly higher levels of NO_x emissions than those burning conventional diesel fuel [78-88]. However, recent studies [82,84,85] suggest that there are as many as 3 or 4 distinct changes in the combustion process when conventional diesel fuel is replaced by biodiesel fuel or oxygenated additives, and it now appears that careful attention to these different features could avoid increased NO_x emissions while retaining the reduced soot production when biodiesel fuel is used. This subject remains a subject of continuing research.

BIOFUELS AUTOIGNITION AND OXIDATIVE STABILITY

Thermal autoignition plays a major role in practical combustion systems [93,94]. Octane Number (ON) measures ignitability and knocking tendency of SI engine fuels, and Cetane Number (CN) measures ignitability of diesel fuel. Fuels with high values of CN and low values of ON ignite easily. The value of ON or CN of any fuel is defined by finding the relative amounts of Primary Reference Fuel (PRF) that shows the same ignition behavior in a carefully defined experimental facility as the fuel being tested [60,95]. Both the ON and CN scales have one PRF that is very easily ignited, *n*-heptane for SI (ON = 0) and *n*-hexadecane for diesel engines (CN = 100), and each scale has a PRF that is difficult to ignite, *iso*-octane for SI (ON = 100) and 2,2,4,4,6,8,8-heptamethyl nonane (or *iso*-cetane) (CN = 15) for diesel engines. For example, if the ignition of a sample of fuel in an octane number test facility ignites at the same time as a mixture that contains 72% *iso*-octane and 28% *n*-heptane, then the ON of the sample fuel is equal to 72. Extended tabulations of ON determinations [61] and CN determinations [32-34] of specific hydrocarbon and other fuel components are available. Extensive kinetic modeling studies [96-100] have been able to provide detailed chemical kinetic reaction mechanisms for these PRFs, and the influences of fuel molecule size and structural features such as straight-chain, branched chain, cycloparaffin, and aromatic fuel structure have become well established.

The five individual biodiesel fuel components shown in Table 1 have very different CN values. The saturated methyl stearate has CN = 101, methyl oleate (with one C=C double bond) has CN = 59, methyl linoleate (two C=C double bonds) has CN = 38, methyl linolenate (three C=C double bonds) has CN = 23 and for the smaller saturated molecule, methyl palmitate has CN = 86. These CN values show clearly that increased numbers of C=C double bonds reduce rates of ignition and CN values, and this correlation has been described previously [32,58].

In SI, diesel and HCCI engines with either conventional or bio-derived fuels, reactive fuel/oxidizer mixtures begin to react at relatively low temperatures and are heated steadily by compression due to piston motion and, in the SI engine, by additional compression due to flame propagation following spark ignition. At temperatures that are still quite low, about 700K, an important class of reactions becomes important, consisting of addition of molecular oxygen O_2 to the radicals R produced by abstraction of H atoms from the fuel. Starting with the RO_2 adduct, the complex series of elementary reactions include transfers of H atoms via isomerization pathways within the adduct, a variety of decomposition reactions to smaller species, and addition of more O_2 molecules. The overall roadmap of these reactions is summarized in Fig. 4.

Most of these reaction pathways provide chain propagation, but chain branching is accomplished after addition of the second O_2 , followed by the decomposition of the keto-hydroperoxide to produce multiple OH and other radical species. At low temperatures, below about 850K, the RO_2 and the O_2QOOH adducts are relatively stable and the overall reaction can proceed quite rapidly and produce a true ignition. However, as the temperature increases, the equilibrium of the O_2 addition shifts back toward the dissociated reactants,

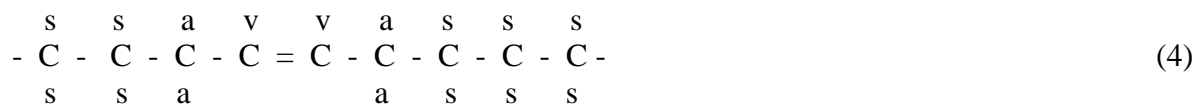


and the low temperature chain branching sequence is extinguished.

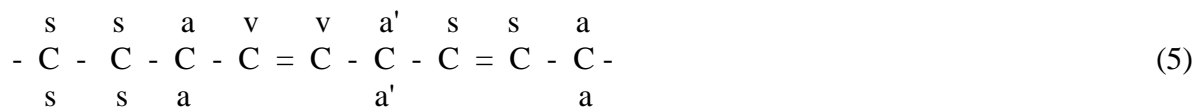
This family of reaction pathways is called "alkylperoxy radical isomerization", or "low temperature oxidation" or "cool flame chemistry", and for fuels which experience these reaction sequences, these pathways provide significant amounts of fuel consumption and temperature increases of as much as 200K, which can lead to significantly advanced final ignition. As a result, fuels which experience low temperature oxidation ignite earlier than fuels that do not.

The general features of the low temperature oxidation mechanism have been studied extensively and summarized by Pollard [101], and the theory of thermokinetic interactions that underlies cool flames were reviewed by Griffiths and Scott [102]. More recently, chemical kinetic reaction mechanisms have been developed to study these systems computationally [18,19,97,98,103], making it possible to identify areas that need further refinement [104-106]. Numerical modeling has been valuable in establishing specific fuel structure factors that explain in fundamental terms the chemical basis for octane numbers and cetane numbers [94].

Extension of this kinetic modeling approach to autoignition of biodiesel fuels adds a structural element not previously involved with most petroleum-based hydrocarbon reference fuels. Several kinetic modeling groups have developed kinetic models for ignition and combustion of biodiesel fuels [40,42,44,107], and most of the kinetic information needed for conventional hydrocarbons can be used directly in the biodiesel models. However, the important bonds in petroleum-based hydrocarbon fuels are single bonds, but when biodiesel fuels are involved, most of the fuel species include C=C double bonds, often multiple such bonds. We can write out the structure of a portion of methyl oleate, with one C=C double bond:



and the same portion showing two C=C double bonds and the different types of C-H bonds in methyl linoleate. The extension to the linolenate is similar to the linoleate.



There are two major implications of these structures. First, the C-H bonds at the allylic sites marked by (a) are significantly weaker than the secondary sites marked by (s), and the C-H bonds of the *bis*-allylic methylene group (a') between the two double bonds are even weaker, resulting in preferential abstraction of these weakest bonded H atoms and producing a radical at the allylic sites in methyl oleate and at a *bis*-allylic site in methyl linoleate or methyl linolenate. These then become the primary sites for addition of O₂, which ordinarily would then initiate a sequence of alkylperoxy radical isomerization reactions and low temperature chain branching as summarized above. Considerable theoretical and experimental attention has been given to the energetics of these R + O₂ addition/dissociation reactions [104,108-110] and their variations as the size and structure of the hydrocarbon radical changes.

However, the second implication of the biodiesel molecule structure in Eqs. 4 and 5 is that, just as noted for the C-H bonds at that location, the bond energy of the R-O₂ at these sites is much less than corresponding R-O₂ bonds at ordinary secondary sites. For example, the R-O₂ bond energy at a secondary site is about 38 kcal/mol, the R-O₂ bond energy at the allylic site is much lower at about 27 kcal/mol, and the R-O₂ bond energy at the *bis*-allylic site is lower still at about 16 kcal/mol [111]. This very low bond energy means that the O₂ is so weakly bound that the RO₂ almost immediately decomposes back to its reactants at compressed gas conditions in engines. As a result, very little low T reactivity is initiated at this site due to the very short lifetime of the adduct, and since this R was preferentially produced by H atom abstraction from the fuel, this fuel species reacts very slowly at low temperatures. Computed thermal autoignition calculations at 13.5 bar and stoichiometric mixtures of each biofuel shown in Table 1 produced the ignition time delays shown in the last row of Table 1, showing clearly the inverse relation between ignition delay times and CN or DN. Uncertainties on the absolute R-O₂ bond energies are still as large as 4 - 8 kcal/mol, and better precision is needed. Earlier we discussed the oxidation stability of biodiesel fuels and how that stability was measured by the Iodine

Number. The explanation for this instability is the extremely low bond energy of the bis-allyl C-H bonds in methyl linoleate and methyl linolenate, which are the main source of this fuel storage instability, because those H atoms are abstracted at appreciable rates even at room temperature. Radicals produced in this way cannot decompose readily into smaller fragments, due to the low temperature, so they recombine into much larger, more viscous molecules that clog filters and hoses. In addition to the R-O₂ bond energies that affect the equilibrium constants of these addition reactions, rates of isomerization that transfer H atoms radicals, and bond energies for quasi-stable intermediates, such as the ketohydroperoxides and hydroperoxides, are poorly determined and chemical theory is making significant contributions [105]. Zhang and Dibble [112] reported a recent study that evaluated rates of alkylperoxy radical isomerization reactions with a C=C double bond as part of an intermediate transition state ring, showing that such isomerizations, which would be particularly relevant to low temperature reactivity of biodiesel fuels, are not strongly inhibited as previously believed. All of these studies are essential to determine ratios of chain branching to chain propagation in these low temperature processes. A further complication is that, to date, no QOOH species has been detected during low temperature hydrocarbon kinetic processes, yet these species play central roles in every existing kinetic mechanism of these processes, both for biodiesel fuels as well as for petroleum-based hydrocarbon fuels.

Even for small fuel molecules such as butanols or pentanols, some low temperature reactivity can be found, and Welz et al. [113] recently examined these reaction pathways for n-butanol and isobutanol. The potential energy surface for the reaction of the 1-butyl radical from n-butane with molecular oxygen can be seen in Fig. 5 from Zador et al. [106], who discuss each of these reaction pathways and how it affects the overall low temperature reactivity of n-butane. Some direct reactions

are shown as dashed lines, the heavy line depicts a direct pathway eliminating HO₂, and the other curves indicate the energies of the sequence of structures that occur between n-butyl radicals + O₂ and final products. This example is much simpler than the corresponding analysis for a biodiesel fuel radical would be, with 17 C atoms as well as the methyl ester moiety. As the capabilities of theoretical methods grow, this should be a very fruitful area for new research. In the meantime, kinetic models make order-of-magnitude estimates based on structural similarities such as the type of C-H or C-O₂ bond being made or broken, or the size of the transition state ring through which a reaction occurs.

Like all engine fuels, biofuels react as the temperature increases from initial room temperature levels to ignition when they reach H₂O₂ decomposition temperature at about 1000K, passing rapidly from H₂O₂ decomposition into OH + OH to a higher temperature ignition.



The important Reaction 6 [93,114] converts the H₂O₂ decomposition temperature into a virtual "trigger" temperature, and this ignition event raises the temperature to a value of about 1200K where the final ignition occurs. Each fuel produces different amounts of reaction and heat release over the NTC region; fuels that have more reaction at these conditions will get to this trigger temperature earlier than other fuels with less low T reactivity. Those fuels that react the most at low T have high CN values when burned in diesel engines and low ON values burned in SI engines.

A challenge to advances in fundamental properties of biodiesel fuels is that the very large molecules have low vapor pressures under normal conditions for careful experiments, and the large number of atoms in each molecule make them difficult to study using *ab initio* computational methods. New techniques are gradually being developed to deal with these and other difficulties. The aerosol shock tube [38,39] is an example where the final vaporization of large molecular weight fuels can be accommodated by using the incident shock wave to vaporize a liquid fuel aerosol. Weng et al. [115]

have used tunable synchrotron vacuum ultraviolet (SVUV) photoionization mass spectrometry (PIMS) to study pyrolysis of wood samples (i.e., poplar) and compare production of different types of lignins, together with cellulose and hemicellulose products at different temperatures, information which can lead to more understanding of biomass conversion to more useful fuels.

CONCLUDING REMARKS

Society is responding to economics, politics and global climate change in trying to find renewable fuels for the future. Over millenia, plants have shown that they are very good at converting sunlight to biomass, so fuels made from biological systems are a clear candidate to satisfy energy needs of the future. Today, science in the form of laboratory experiments, advanced optical diagnostics, quantum theory and electronic structure, and high performance computing are assisting in the analysis of fuels produced from biomass and their combustion characteristics, to assess their potential as eventual replacements for fuels derived primarily from petroleum. These advanced analytical tools are greatly accelerating the search for new energy sources, and the present review provides some highlights of recent progress.

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Figure captions

Figure 1. Structural diagrams of major components of soy, rapeseed and many other biodiesel fuels

Figure 2. Three types of internal combustion engine in common use

Figure 3. Schematic diagram of combustion zones in a diesel combustion jet [65], courtesy of J. Dec

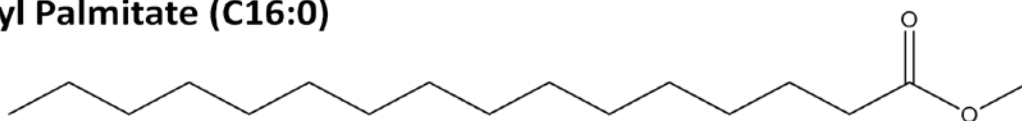
Figure 4. Reaction pathways in the low temperature regime

Figure 5. Schematic potential energy surface for the reaction of n-butyl radical with O_2 [106],
courtesy of C.A. Taatjes.

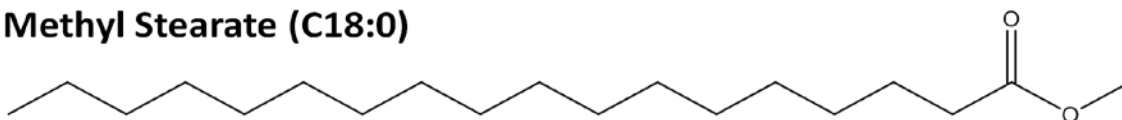
Table caption

Table 1. Composition of selected biodiesel methyl ester fuels, using fuel species from Fig. 1.

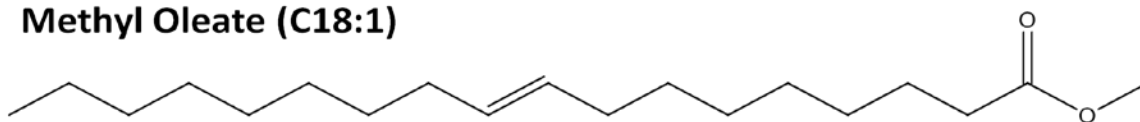
Methyl Palmitate (C16:0)



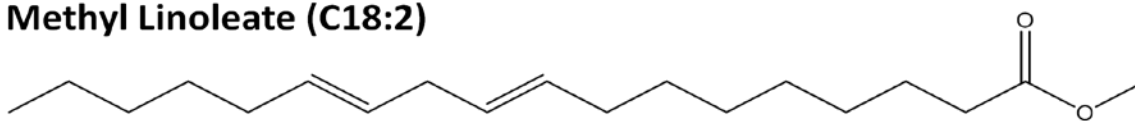
Methyl Stearate (C18:0)



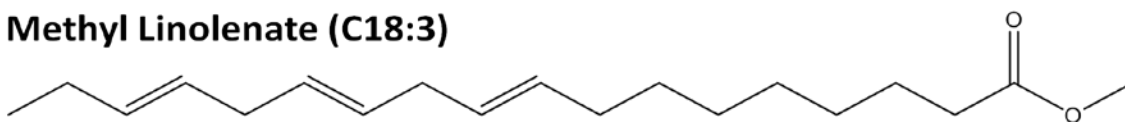
Methyl Oleate (C18:1)



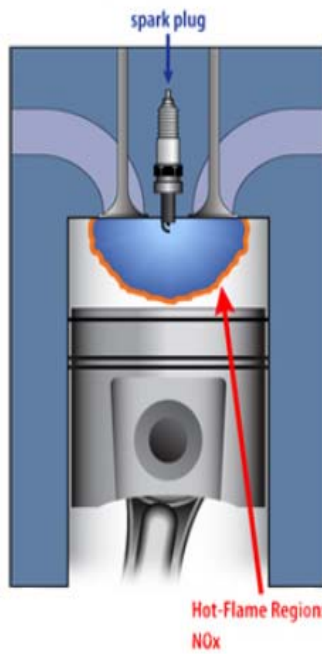
Methyl Linoleate (C18:2)



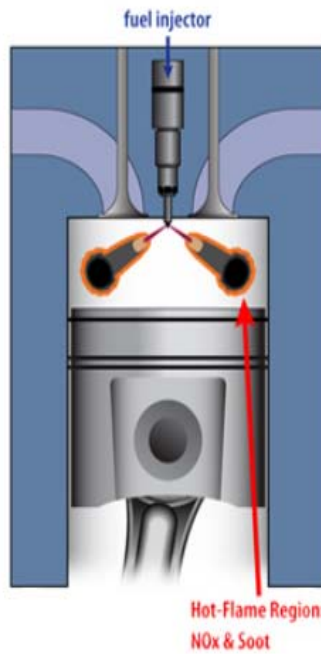
Methyl Linolenate (C18:3)



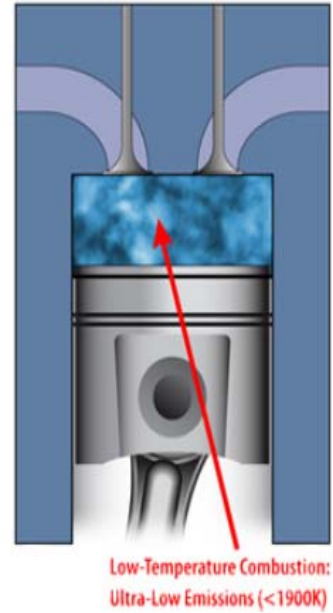
Gasoline Engine (Spark Ignition)

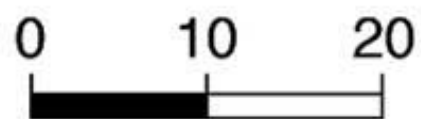
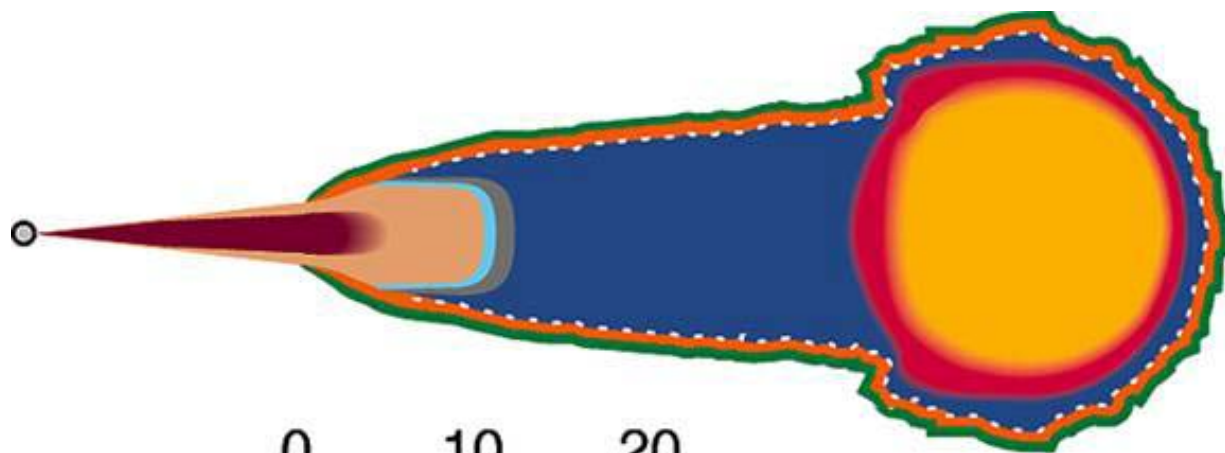


Diesel Engine (Compression Ignition)


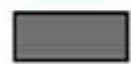




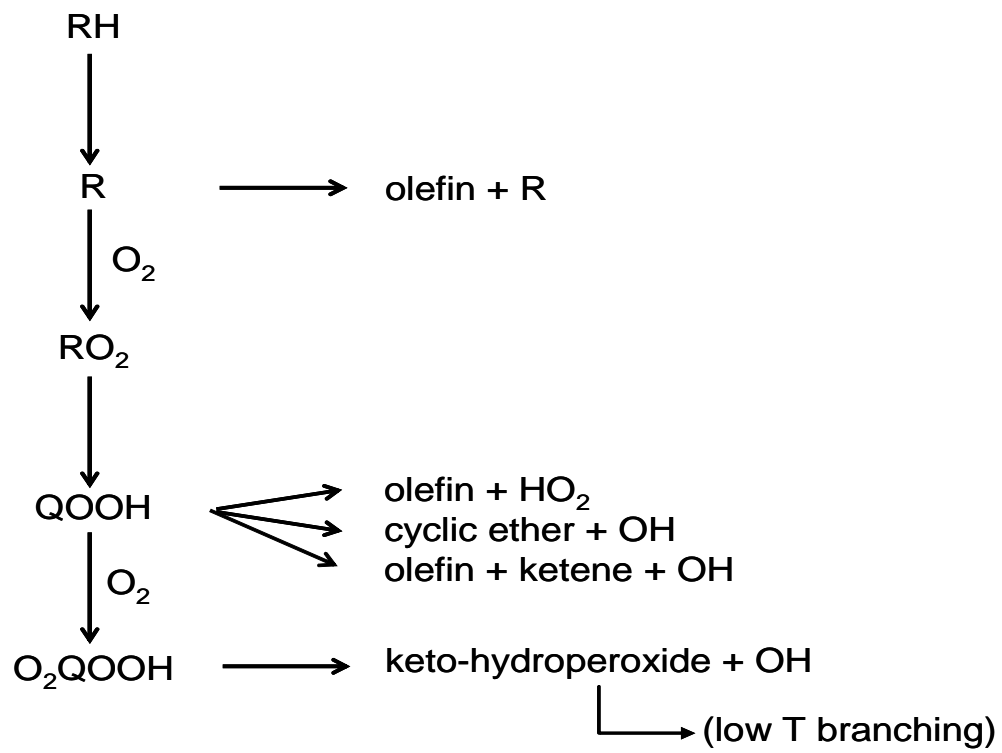
HCCI Engine (Homogeneous Charge Compression Ignition)

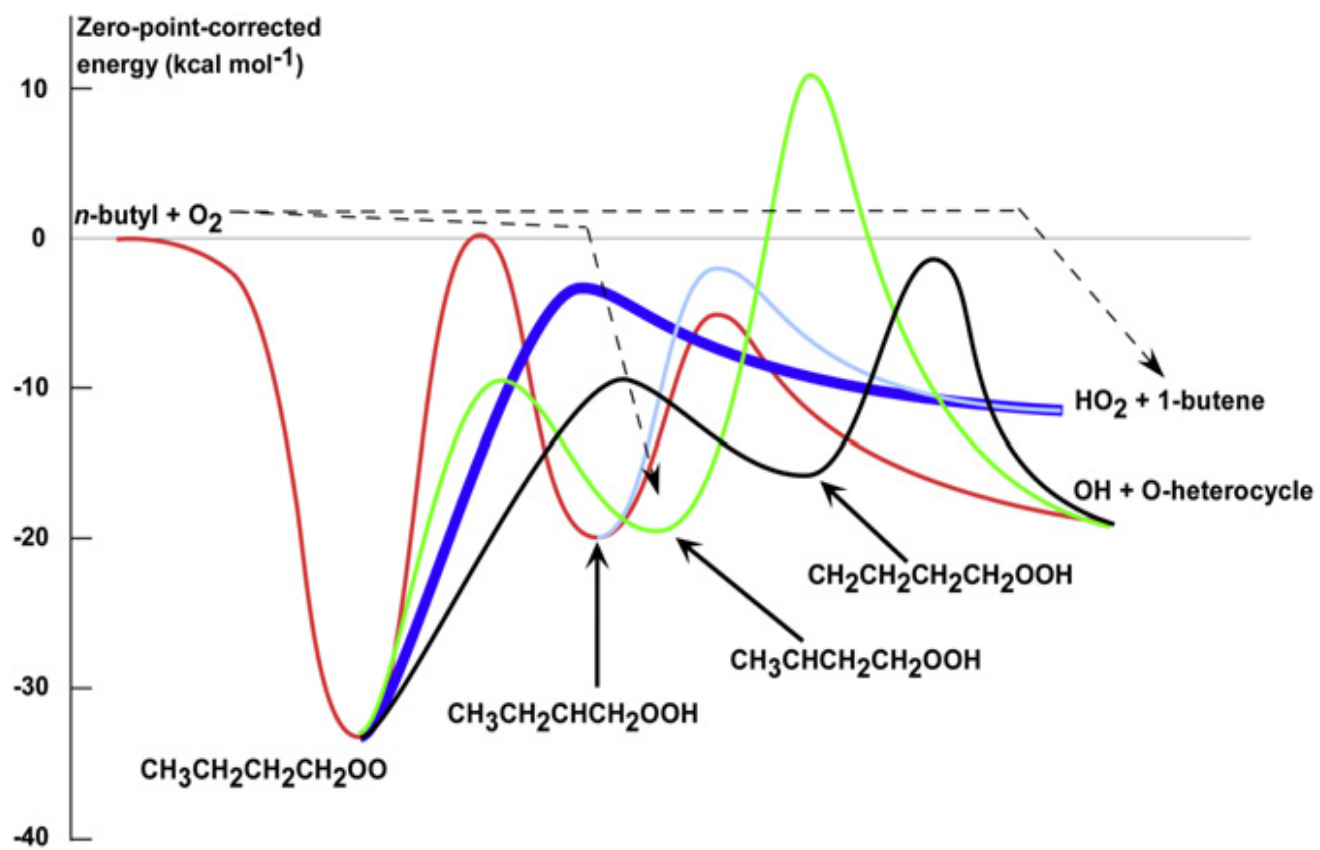




Scale (mm)

-  Fuel-Rich Premixed Flame
-  Initial Soot Formation
-  Thermal NO Production Zone
-  Soot Oxidation Zone





	sun	saff	linseed	jatropha	cotton	corn	olive	tallow	palm	peanut	soy	rapeseed
palmitate	7	7	7	4	23	10	13	28	46	11	8	4
stearate	5	2	1	8	3	4	4	22	4	8	4	1
oleate	19	13	19	49	20	38	72	46	40	49	25	60
linoleate	68	78	19	38	53	48	10	3	10	32	55	21
linolenate	1	0	54	1	1	0	1	1	0	0	8	14
CN	49	50	39	58	51	49	55	58	62	54	47	54
DN	158	169	219	128	129	134	95	55	60	113	159	144
tign-ms	6.7	6.9	10.2	6.0	6.0	6.5	6.2	4.6	4.6	6.1	6.9	7.0